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Lubricant From a Gas-Turbine
Engine Test by Size-Exclusion
Chromatography**

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Analysis of a MIL-L-27502 Lubricant From a Gas-Turbine Engine Test by Size-Exclusion Chromatography

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Scientific and Technical
Information Branch

SUMMARY

Size exclusion chromatography (SEC) utilizing a μ -Bondagel and μ -Styragel columns with a tetrahydrofuran mobile phase was used to determine the chemical degradation of lubricant samples from a gas-turbine engine test. A MIL-L-27502 candidate, ester-based lubricant was run in a J57-29 engine at a bulk oil temperature of 216° C. In general, the analyses indicated a progressive loss of primary ester, additive depletion, and formation of higher molecular weight material. An oil sample taken at the conclusion of the test showed a reversal of this trend because of large additions of new oil. The high-molecular-weight product from the degraded ester absorbed strongly in the ultraviolet region at 254 nanometers. This would indicate the presence of chromophoric groups. An analysis of a similar ester lubricant from a separate high-temperature bearing test yielded qualitatively similar results.

INTRODUCTION

Currently used gas-turbine engine lubricants for most military aircraft must meet either specification MIL-L-7808 H (use temperature range, -54° to 163° C) or MIL-L-23699 C (-40° to 177° C) (refs. 1 and 2). New or improved engine oils having higher bulk temperature limits will be needed for advanced engines (ref. 3). A higher temperature specification (MIL-L-27502) has been issued for bulk oil temperature limits of -40° to 220° C (ref. 4).

These specifications require that all candidate fluids pass a 100-hour, full-scale engine endurance test. Tests are conducted at the Aero Propulsion Laboratory of the Air Force Wright Aeronautical Laboratories, WPAFB, Ohio, in a J57-29 engine at a prescribed series of test cycles under various throttle settings. A posttest inspection is conducted on the disassembled engine. In addition, periodic oil samples are taken for posttest analysis. These include standard tests of physical and chemical properties, elastomer compatibility, corrosion, deposition, and lubrication characteristics. Changes in these parameters are usually indicative of the amount of fluid degradation that has occurred.

Recently, the development of high-pressure liquid chromatography has afforded another method for the analysis of the chemical changes of liquid lubricants (refs. 5 and 7). Size exclusion is a form of liquid chromatography in which solute molecules are separated according to size by permeation into a solvent-filled matrix.

The objective of this work was to determine the chemical degradation of gas-turbine engine lubricant by analyzing samples from a full-scale engine (J57-29) test by size exclusion chromatography. Samples were taken from a 216° C bulk oil temperature test using a MIL-L-27502 candidate lubricant.

Mr. G. A. Beane, of the Lubrication Branch of the Air Force Wright Aeronautical Laboratories, supplied the engine oil samples and documentation.

APPARATUS AND PROCEDURE

Liquid Chromatograph

A Waters Model 244 liquid chromatograph was used. The unit is combined with an ultraviolet (UV) absorbance detector and a differential refractive

index detector (RI). Abbreviations used in this report and some definitions appear in the appendix. The UV detector monitors the absorbance at a wavelength of 254 nanometers at sensitivities ranging from 0.005 to 2.0 absorbance units full scale (AUFS). The refractometer is sensitive to all compounds that differ in refractive index from the mobile phase. It will detect changes in the RI as small as 10^{-7} RI units throughout the RI range of 1.00 to 1.75.

For these studies the chromatograph was setup in the size exclusion mode. One E-Linear μ -Bondagel, one (500 Å), and two (100 Å) μ -Styragel columns were used. A schematic flow diagram of the liquid chromatography system is shown in figure 1. Sample injection size was 150 microliters. Samples were prepared by dissolving 40 microliters of lubricant in 3 milliliters of tetrahydrofuran.

Solute molecules are separated as a result of their permeation into the solvent-filled matrix in the column packing. This is schematically illustrated in figure 2. Here, an idealized sample containing large and small molecules is shown passing through a size exclusion column. The smaller molecules are able to penetrate into the pore structure of the packing, thus retarding their rate of travel through the column. The larger molecules are excluded and travel at a faster rate. Ideally, a complete separation will eventually be effected. In these studies tetrahydrofuran (THF) was the solvent at a flow rate of 1 milliliter per minute. Figure 3 contains a calibration curve for column retention time as a function of molecular weight for various standards. Table I contains the exact retention time for each standard.

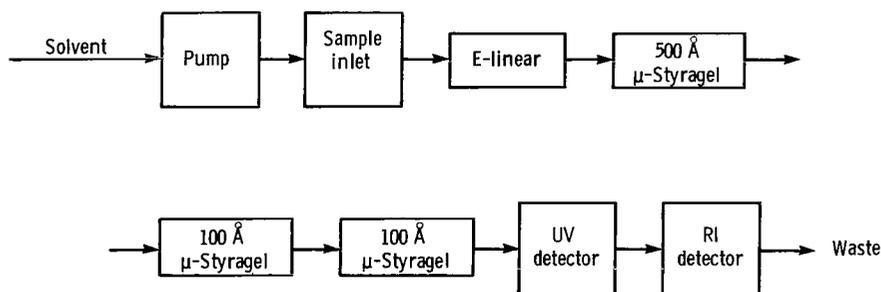


Figure 1. - Flow diagram for liquid chromatographic system.

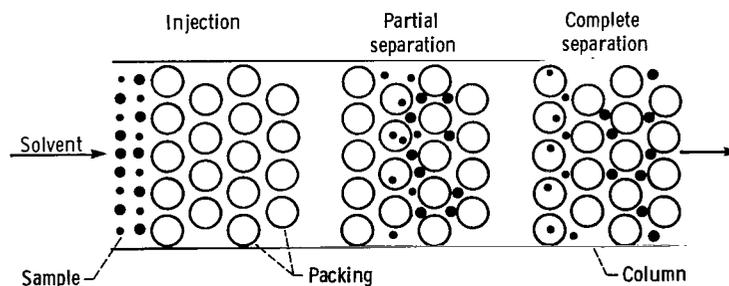


Figure 2. - Schematic diagram of size exclusion chromatography.

TABLE I. - COLUMN RETENTION TIMES FOR VARIOUS MOLECULAR WEIGHT CALIBRATION STANDARDS

Standard ^a	Molecular weight	Retention time, min
Polystyrene	2.7×10^6	14.5
Polystyrene	3.5×10^4	15.6
Polystyrene	2.4×10^3	17.9
Pentaerythritol tetraheptanoate	580	21.4
D1-2-Ethylhexyl sebate	420	22.5
Diphenylether	170	28.2

^a150 microliter injection.

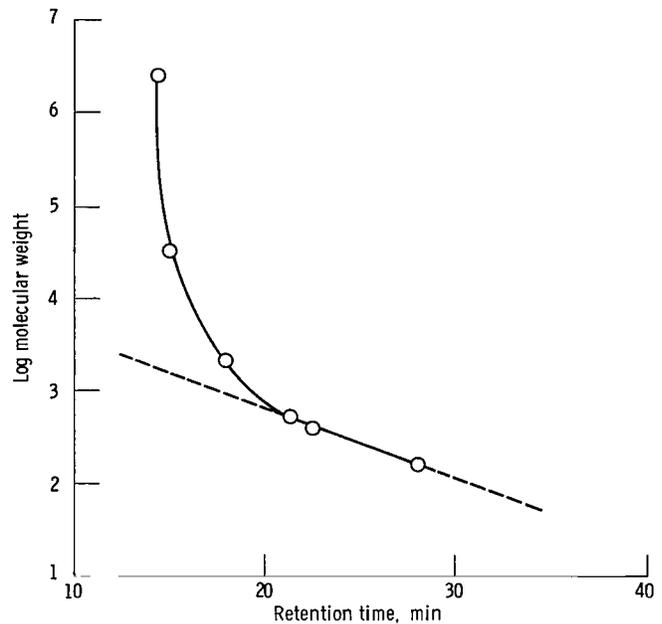


Figure 3. - logarithmic molecular weight versus retention time calibration curve for 1 E-linear, one 500-Å, and one 100-Å columns at a flow rate of 1 ml/min. Mobile phase, tetrahydrofuran.

TABLE II. - SUMMARY OF J57-29 ENGINE TEMPERATURE TEST CONDITIONS FOR MIL-L-27502 CANDIDATE FLUID

	Temperature, °C
No. 1 bearing outer race	174
No. 5 bearing outer race	242
No. 3 seal support	279
No. 6 cover	282
Bulk oil	216
Scavenge temperature	204

Lubricant Sampling

In this test lubricant samples were taken at pretest and at 30, 65, and 100 hours (test conclusion). All samples were taken from the engine tank valve immediately after engine shutdown. Approximately 1 liter of oil was drawn to clear the line before taking a sample. This oil was returned to the tank before topping off. The total lubricant fill for this system was approximately 55 liters (14.5 gal).

J-57-20 Engine Test

The U.S. Air Force gas-turbine engine test is based on a controlled compressor discharge temperature and consists of 20 cycles. The engine is run for 25 minutes at a power setting that will give a controlled compressor discharge temperature between 316° and 335° C, followed by 5 minutes at idle.

This is repeated 10 times for each 5-hour cycle. The No. 6 sump cover temperature is controlled at approximately 302° C, and the bulk oil temperature at 219° C. The exact temperature conditions achieved appear in table II.

Materials

The ester-base fluid used in this study is a MIL-L-27502 candidate lubricant whose composition is not limited except that organometallic compounds of titanium are prohibited (ref. 4). The base stock is a mixture of Hercules L-78 (90%) and Hercules L-31 (10%). Hercules L-78 contains hindered polyolesters of straight-chain fatty acids (C₅ to C₁₀). Hercules L-31 is a more viscous (higher molecular weight) version of L-78 which contains more polyentaerythritols. Some physical properties of the blended test fluid appear in table III. The additive content of the test fluid is given in table IV.

TABLE III. - TYPICAL PROPERTIES OF FORMULATED ESTER^a TEST FLUID
(MIL-L-27502 CANDIDATE)^b

Kinematic viscosity, m ² /sec (cS), at -	
38° C	3.96x10 ⁻⁵ (39.6)
99° C	7.02x10 ⁻⁶ (7.02)
150° C	2.80x10 ⁻⁶ (2.80)
260° C	1.06x10 ⁻⁶ (1.06)
300° C	^c 8.6x10 ⁻⁷ (0.86)
Pour point, °C	-51
Flashpoint, °C	274
Specific gravity, 25.6° C/15.6° C	0.094
Thermal decomposition (isoteniscope), °C ^e	298
Vapor pressure, Pa, at 220° C	1.33x10 ²

^aBase stock mixture of hindered polyolesters, polyester, and dipentaerythritol esters (ref. 3).

^bManufacturer's data, unless otherwise noted.

^cExtrapolated.

^eMeasured in author's laboratory.

TABLE IV. - ADDITIVE CONTENT OF TEST FLUID
(MIL-L-27502 CANDIDATE)

Description ^a	Function
Complex alkali metal organo-phosphorus compound (ref. 8)	Antioxidant
Diocetyldiphenylamine (type II)	Antioxidant
Proprietary Amine (type I)	Antioxidant
Metal deactivator	Magnesium corrosion inhibitor
Silicone (Dow Corning 200)	Antifoam

^aMore information regarding these additives appears in ref. 3.

RESULTS

Size exclusion chromatograms for the unused MIL-L-27502 candidate lubricant appear in figure 4. The upper trace is from the ultraviolet (UV) detector and the lower from the refractive index (RI) detector. The RI spectrum shows four peaks. A primary peak is centered at a molecular weight (MW) of about 600, and two higher molecular-weight peaks are at about 1000 and 2400. A small shoulder occurs at a MW = 420. The UV trace indicates three

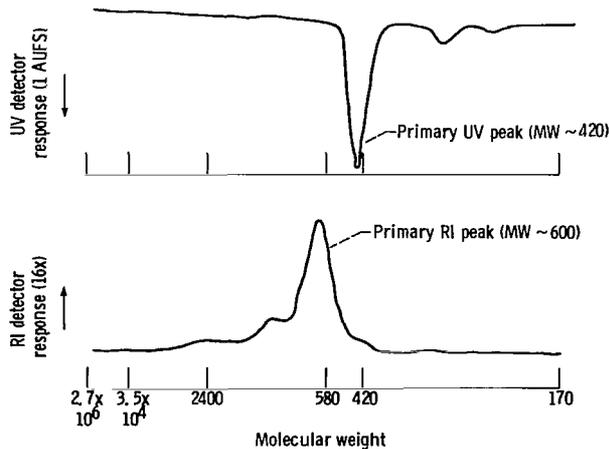


Figure 4. - Size exclusion chromatograms for unused MIL-L-27502 lubricant.

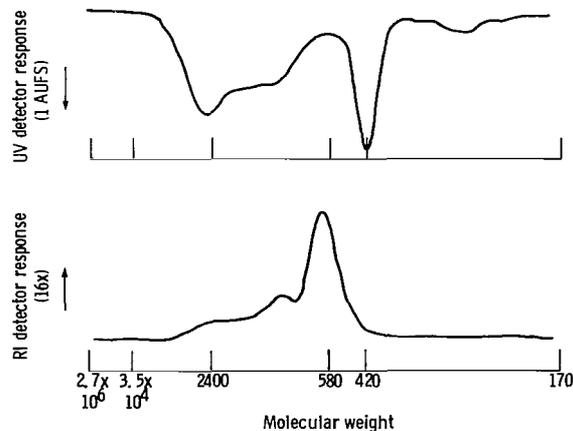


Figure 5. - Size exclusion chromatograms for MIL-L-27502 lubricant from J-57 engine test, 30-hr sample.

components: a primary peak at a MW = 420 and two smaller peaks at MW = 300 and 200.

Figure 5 shows chromatographic results for an engine oil sample taken at 30 hours. The RI chromatogram is very similar to the unused oil trace (fig. 4). The primary peak at MW = 600 and the shoulder at 420 have diminished. However, the peaks at 1000 and 2400 have grown. The UV spectrum, however, has changed considerably: The two low-molecular-weight peaks have coalesced into one peak at about 280; the primary 420 peak has diminished; and two large unresolved peaks are now present in the high-molecular-weight region.

Figure 6 shows the chromatographic data for the next engine oil sample at 65 hours. Again, the RI and UV chromatograms are essentially the same as for the unused sample except for continued growth of the 2400 and 1000 peaks and reduction of the 600 and 420 components.

The spectrum for the final sample, taken at test conclusion (100 hr), appears in figure 7. Again, as in the previous two samples, similar high-molecular-weight features are present. However, there is less degradation (i.e., less high-molecular-weight material) than in the 65-hour sample (fig. 6). A summary of the spectra for the unused, 30- and 65-hour samples

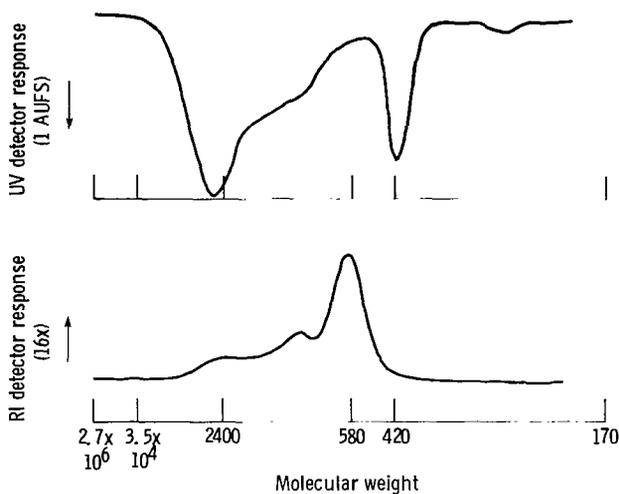


Figure 6. - Size exclusion chromatograms for MIL-L-27502 lubricant from J-57 engine test. 65-hr sample.

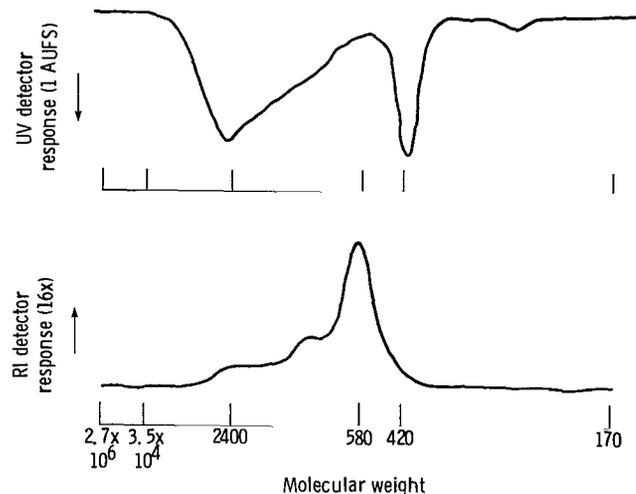


Figure 7. - Size exclusion chromatograms for MIL-27502 lubricant from J-57 engine test. 100-hr sample; test conclusion.

appears in figure 8(a) for the RI detector and in figure 8(b) for the UV detector. The gradual buildup of the high-molecular-weight material and decrease of the primary peaks are evident.

To quantify some of these changes, the area under each trace was measured by a planimeter. Then each trace was arbitrarily broken into three regions. These consisted of a primary peak and low- and high-molecular-weight regions. Note that these regions must be compared on each mode (RI or UV) separately, because the detectors sense different chemical species. The area percents for the various regions are plotted for each test sample in figures 9 and 10. In both figures the decrease in the primary and low-molecular-weight regions and the increase in the high-molecular-weight region are evident in both the 30- and 65-hour samples. The reversal in trends mentioned earlier for the 100-hour sample is also evident.

DISCUSSION

SEC Analysis - Unused Fluid

The UV data on the unused lubricant (upper trace, fig. 4) yields information on the additive content of the lubricant. Diphenyldioctylamine (DODPA) contains an auxochromic amino group and chromophoric aromatic group. The aromatic benzene ring has a broad absorption band in the near ultraviolet between 230 and 270 nanometers. This absorption is associated with $\pi \rightarrow \pi^*$ electronic transitions. Substitution of an auxochromic group (i.e., $-\text{NH}_2$) usually increases the intensity of absorption and shifts it to a longer wave-length (bathochromic shift) (ref. 9). For example, benzene (C_6H_6) absorbs at 254 nanometers with an intensity of ($\epsilon_{\text{max}} = 204$), while aniline ($\text{C}_6\text{H}_5-\text{NH}_2$) absorbs at 280 nanometers ($\epsilon_{\text{max}} = 1430$) (ref. 9). Since DODPA has a molecular weight of 393, it seems likely that the primary UV peak at 420 can be assigned to this additive. DODPA was probably present at a 1 percent by weight concentration (ref. 3).

The second amine present in the formulation was a proprietary type I antioxidant. Reference 3 lists six aromatic amines (four indazoles and two pyridines) studied at low concentrations (0.01 to 0.3 wt.%). The small peak

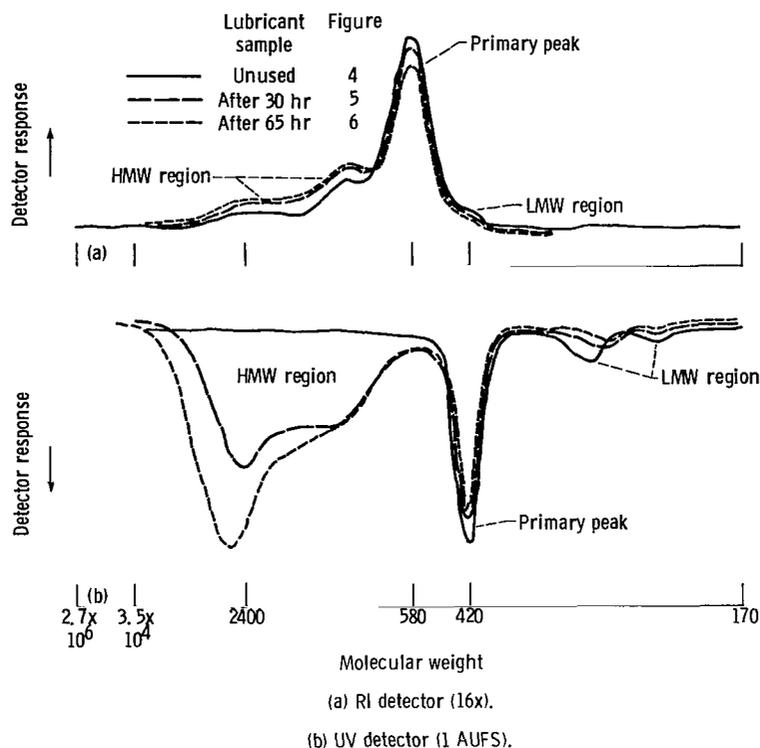


Figure 8. - Summary of size exclusion chromatograms for unused, 30- and 65-hr samples.

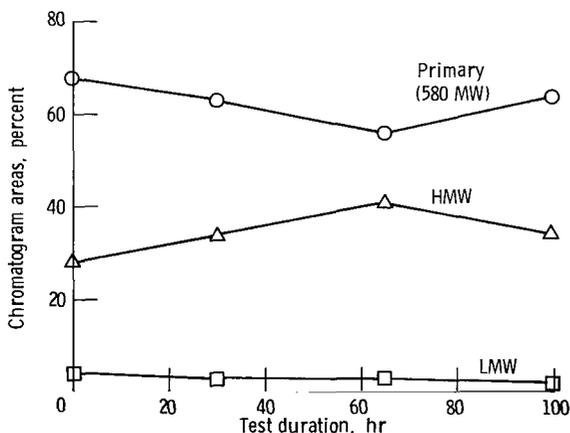


Figure 9. - Chromatogram areas for primary, high molecular weight (HMW) and low molecular weight (LMW) peaks from refractive index detector.

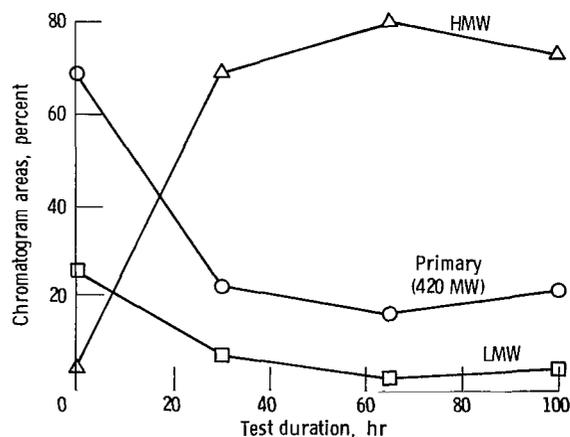


Figure 10. - Chromatogram areas for primary, high molecular weight (HMW) and low molecular weight (LMW) peaks from ultraviolet detector.

in the UV trace (fig. 4) at an approximate molecular weight of 300 can be assigned to one of these amines. The third small peak at lower molecular weight is probably one of the remaining additives or a THF artifact. (Oxidation of THF during sample preparation sometimes produces small amounts of products in this molecular weight region.)

The primary peak in the unused RI trace at MW = 600 is the ester base-stock. The peaks at 2400, 1000, and 420 are presumed to be higher and lower molecular weight basestock components.

30-Hour Sample

The most striking change in the UV spectrum of the 30-hour test sample is the appearance of a broad peak in the high-molecular-weight region. This, no doubt, is caused by the generation of oxidized ester products. The fact that only a small change occurred in the RI region is not surprising. Esters produce products containing carbonyl groups conjugated with one or more double bonds (ref. 8). Conjugation decreases the energy required to bring about electronic transitions. Thus, strong absorption occurs in the near ultraviolet. These $\pi \rightarrow \pi^*$ transitions occur at longer wavelengths. Because of this marked difference in absorbtivity, it is very difficult to relate the size of this peak to the amount of material actually present. However, relative comparisons can be made (figs. 9 and 10).

65-Hour Sample

The 65-hour sample shows more ester degradation than the 30-hour sample. Increases are denoted by the amount of high-molecular-weight material in both traces (fig. 6). In addition, decreases are observed for the primary additive peak in the UV and the primary ester peak in the RI.

100-Hour Sample

Suprisingly, the 100-hour sample showed less degradation than the previous sample. An examination of the oil additions during the engine test (fig. 11) revealed that the continually increasing rate of oil additions is responsible for the apparent reversal in ester degradation. The large additions are probably related to the volatility of the fluid at the high-engine test temperatures.

Correlation with Other Investigators

Ali, et al., (ref. 8) reported on the chemical degradation of ester lubricants. Using a similar analytical technique (gel permeation chromatography), they found different molecular-weight fractions related to degradation. For pentaerythritol tetraheptanoate (PEC₇), which is chemically similar to the ester basestock of this paper, two high-molecular-weight fractions of 860 and 1900 to 2400 MW were reported. In addition, a low-molecular-weight fraction of <220 was shown for di-2-ethylhexylsebacate (said by the authors to be representative of all other esters studied). The suggested mechanism of breakdown was the initial generation of low-molecular-weight material, which then began a series of polymerization steps to a dimer (fraction 2) and finally oligomers (fraction 1). However, the data for the PEC₇ ester on the distribution of material in the various fractions shows nothing for fraction 3 (LMW material).

The data from our work show no increase in the low-molecular-weight material (RI trace) corresponding to Ali's fraction 3 with increasing ester degradation. In fact, the greatest amount of low-molecular-weight material in our data occurred in the unused oil sample. So the theory proposed by Ali, et al., (ref. 8) that low-molecular-weight material is formed which subsequently feeds the polymerization reaction is not confirmed here. However, it is realized that the time between taking a sample and analysis is

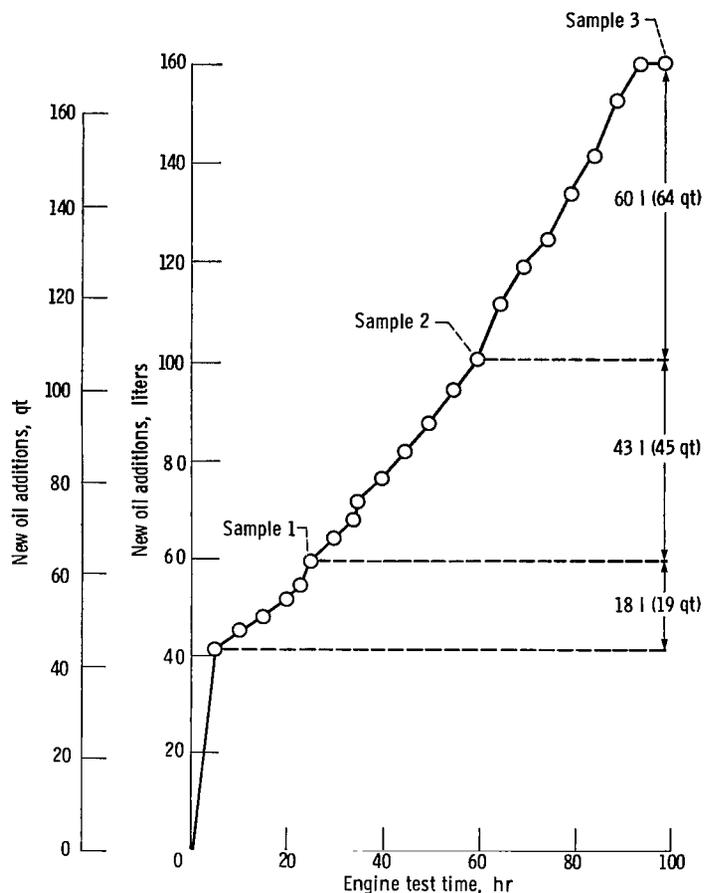


Figure 11. - New oil additions during J-57 100-hr engine test.

important. The samples from the present study were more than a year old. Reaction of low-molecular-weight active species could have taken place.

Comparison of the high-molecular-weight peaks shows similarities. The high-molecular-weight peaks of our data (MW = 1000 and 2400) compare favorably with Ali's (MW = 860 and 1900 to 2400) fractions. This apparent oligomeric material could be the precursor of high-molecular-weight sludge and varnish. The SEC analysis of our work does show that the initial high-molecular-weight material is eluted near the MW = 35 000 calibration point.

Bearing Test Samples

Essentially the same ester formulation studied here was run in a 100-hour bearing test at type II conditions (ref. 10). These conditions refer to an oil inlet temperature of 204° C, a bearing race temperature of 260° C, and a bulk oil temperature of 218° C. The gel permeation chromatogram for the sample taken at test conclusion appears in figure 12. The oil consumption rate in this test was 38.5 cubic centimeters per hour, which corresponds to only about a 3.8 liters (4-qt) addition during the test. It is not surprising, therefore, that this chromatogram shows a great deal more degradation (loss of primary ester and increases of high-molecular-weight material) than the engine test samples. However, the chromatograms are

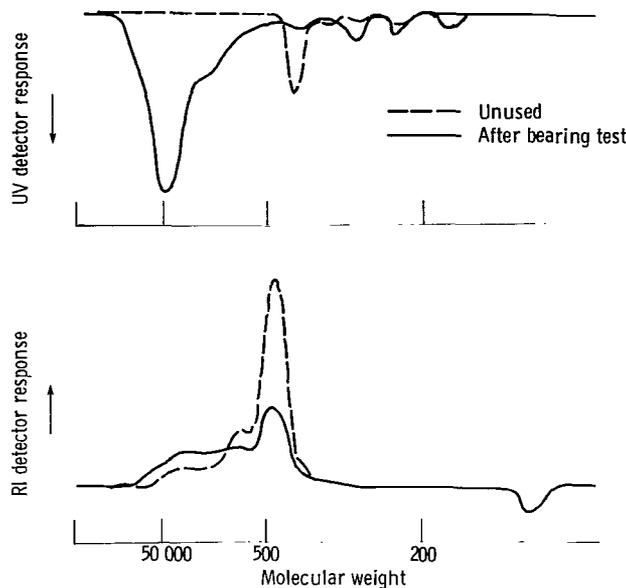


Figure 12. - Gel permeation chromatogram of a formulated ester from a 100-hr bearing test. Bulk oil temperature 218^o C. (Bearing test from ref. 10.)

qualitatively similar. Comparing the UV data of figure 6 (65-hr sample) with those of figure 12 indicates a shift in the distribution of the high-molecular-weight material. There appears to be more material at a higher molecular weight (approximately 50 000). Varnish deposits were observed on bearing disassembly. This high-molecular-weight material may be the precursor for varnish formation.

SUMMARY OF RESULTS

Size exclusion chromatography has been used to determine the chemical degradation of ester oil samples (MIL-L-27502) from a high-temperature, J-57-29, gas-turbine engine test. The following results were obtained:

1. In general, progressive loss of primary ester, additive depletion, and formation of higher molecular weight material occurred as a function of engine test time.

2. The high-molecular-weight material from the degraded ester absorbed strongly in the ultraviolet region at 254 nanometers, indicating the presence of chromophoric groups.

3. Chromatographic analysis of a similar ester oil sample from a high-temperature bearing test yielded qualitatively similar results to those obtained on the engine oil samples.

4. The test sample taken at test conclusion showed less degradation than previous samples because of large additions of new oil during the latter stages of the test.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, June 11, 1982

APPENDIX - DEFINITION OF TERMS

Auxochrome - a saturated group which, when attached to a chromophore, alters both the wavelength and the intensity of the ultraviolet absorption maximum.

Bathochromic Shift - The shift of ultraviolet absorption to a longer wavelength due to substitution or solvent effects.

Chromophore - a covalently unsaturated group responsible for electronic absorption.

Size exclusion chromatography (SEC) - a form of liquid chromatography in which solute molecules are separated according to size by permeation into a solvent-filled matrix.

μ -Bondagel - a commercial column of controlled porosity silica with permanently bonded ether phase used in size exclusion chromatography.

μ -Styragel - a commercial column of highly crosslinked styrene divinylbenzene gel used in size exclusion chromatography

$\pi \rightarrow \pi^*$ - transition of a π -electron to a higher energy orbital.

ABBREVIATIONS

AUFS	absorption units full scale
DODPA	dioctyldiphenylamine
GPC	gel permeation chromatography
HMW	high molecular weight
LMW	low molecular weight
PEC ₇	pentaerythritol tetraheptanoate
RI	refractive index
THF	tetrahydrofuran
UV	ultraviolet
ϵ_{\max}	molar absorptivity

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